

The University of Chicago

GUAVA AND APPLE PECTIN
A STUDY OF THEIR CHEMICAL
AND GELATION PROPERTIES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE BIOLOGICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF HOME ECONOMICS AND HOUSEHOLD ADMINISTRATION
SEPTEMBER, 1944

By
ESTHER SEIJO

CHICAGO, ILLINOIS

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INTRODUCTION

Considerable research has been undertaken in the past few years in order to determine the quantitative and qualitative relationship which exists among the three main constituents of jellies: pectin, acid and sugar. Due to such intensive research the processes involved have been understood, and formulas have been devised assuring good products of a definite composition and high sugar concentration. However very little has been done to test these formulas with lower sugar concentration products from different fruits and even different varieties of the same fruit. It is well known that excellent products have always been obtained by some homemakers through a trial and error method yet at present most of the jellies made are not considered excellent products, although their appearance be within our expectations. Either pectin is added to allow more water and less fruit, or such a great excess of sugar is present that the jellies have nothing but an insipid flavor or an exceedingly sweet taste.

The purpose of this study was therefore threefold: first, to determine the quantitative relationship which exists among acid, pectin and sugar in the preparation of low sugar concentration products; second, to determine if available formulas apply or can be made to apply in the preparation of excellent products with low sugar concentration from different fruits and different varieties of the same fruit; and third to study the relation of several physical and chemical properties of the various fruit pectins to their gelation behavior. The first objective was to be accomplished by preparation of synthetic jellies from citrus fruit pectin and the second by preparing extracts from various fruits. The study of the relation of physical and chemical properties of the fruit pectins to their gelation property was to be accomplished by observing the structure of jellies through a dark field or slit-microscope and by carrying on a series of chemical determinations on the pectins extracted from the fruits.

REVIEW OF THE FACTORS WHICH AFFECT THE GELATION OF EXTRACTS

Pectic Substances

Pectic substances found in the intercellular space of the cell walls consist of at least three distinct entities:¹ proto-pectin, the "cementing substance" present in the unripe fruit; pectin, the water soluble modification indispensable for the gelation of extracts;² and pectic acid, the basic unit.

All the pectic substances mentioned above have been shown to yield upon complete breakdown a galacturonic acid nucleus; and according to most observers some galactose, arabinose and acetic acid.³ That the galacturonic acid nucleus is the main constituent is generally agreed upon by all workers but there is no unanimity of opinion regarding the chemical nature of the related compounds. Nanji, Paton and Link⁴ suggest the arabinose, galactose, and galacturonic acid combination formula for pectic acid, while Schneider and Bock⁵ describe pectin as a mere polymer of a galacturonic acid nucleus and consider galactose and acetic acid found among the hydrolytic products, to be merely impurities. Pectin is recognized to be a more or less highly methylated form

¹M. H. Carre, A Critical and Historical Study of the Pectin Substances in Plants, Food Investigation Report No. 3, Department of Scientific and Industrial Research (Great Britain: British Library of Information, 1925), Part 1.

²"Pectinic acid" is term included in the official nomenclature of the Division of Agricultural and Food Chemistry. The term is used for colloidal polygalacturonic acid with more than a negligible proportion of methyl ester groups. Can form gels if of suitably low methoxy content. Chemical and Engineering News, Vol. 22, No. 8 (April 25, 1944), p. 609.

³G. L. Baker and P. B. Myers, Fruit Jellies VI The Role of Pectin, University of Delaware Agricultural Experiment Station Bulletin 149 (1927).

⁴G. L. Baker, "Pectin in Nature and Industry," Scientific Monthly, January, 1935, pp. 48-58.

⁵G. G. Schneider and H. Bock, "The Constitution of Pectic Substances," Berichte, LXX (1937), 1617.

of pectic acid or more likely its polymer.¹ The methylation of pectin is shown by the fact that upon treating a pectic acid solution with dilute alkali, the pectic salt and methyl alcohol are obtained.

The pectin in plants is derived during the ripening process from the protopectin² which is present in the middle lamella of the cell walls as shown by chemical experiments³ and microscopic studies.⁴ It is known⁵ that this is not the only change which occurs in the pectic substances during ripening as the pectin derived will later change into the less soluble form of pectic acid.

Of all the pectic substances mentioned, however, pectin as such is the only form which is capable of forming jellies.⁶ Use of the underripe fruit, rich in protopectin is practically useless for jelly making unless acid is added to bring about a breakdown of the protopectin to pectin.⁷

The amount of pectin which is present in the extracted juice is not the only factor to be considered in jelly making. Recent work⁸ indicates that the quality of the pectin secured is as important a factor in gelation as the quantity which is present.

¹G. L. Baker, "Pectin in Nature and Industry," Scientific Monthly, January, 1935, pp. 4-54.

²M. H. Carre, "An Investigation of the Changes Which Occur in the Pectic Constituents of Stored Fruits," Biochemical Journal, XVI (1922), 704.

³R. H. Dastur and S. D. Agnihorti, "Study of the Pectic Changes in Potato Tubers at Different States of Growth," Indian Journal of Agricultural Science, IV (1934), 430.

⁴M. H. Carre, "Relation of Pectose and Pectin in Apple Juice," Biochemical Journal, XIX (1925), 25.

⁵M. H. Carre, "An Investigation of the Changes Which Occur in the Pectic Constituents of Stored Fruits," Biochemical Journal, XVI (1922), 704.

⁶G. L. Baker, "Extractions and Standards in Fruit Jelly Making," Food Manufacture, IV (May, 1937), 4.

⁷M. H. Carre, "An Investigation of the Changes Which Occur in the Pectic Constituents of Stored Fruits," Biochemical Journal, XVI (1922), 704.

⁸G. L. Baker, "Pectin in Nature and Industry," Scientific Monthly, January, 1935, pp. 4-54.

Just what determines the quality of the pectin has not as yet been definitely proved. Fellenberg¹ believes that the higher the degree of methylation in the pectin the better the quality. No such relation is however admitted by Baker and Myers² who showed that they could deprive pectin of a large amount of its jellying properties without producing any appreciable effect in its methylation. These authors hold that the quality of the pectin is affected by the variation in the method of extraction such as acidity, time, and temperature.

Sugar

Sugar, another important factor in jelly making, is believed to act as a dehydrating agent.³ Experimental work shows however that not only is sucrose as such important in gelation, but that reducing sugars as glucose or levulose are also of value. These sugars may occur naturally in the juice or may be derived from the hydrolysis of the sucrose during boiling. In either case their presence helps to prevent the formation of crystals on the jelly which is usually a saturated sucrose solution.

Acid

Acid in terms of hydrogen ion concentration is the third factor which is recognized as an essential component of jellies. Some investigators believe that the hydrogen ion acts by reducing the negative charges present⁴ which together with the dehydrating effect of sugar precipitates the pectin. According to Norman⁵ however, the effect of acid is to toughen the fibrils of a network formed by the pectin.

¹G. L. Baker, "A New Method for Determining the Jellying Powers of Fruit Juice Extractions," Food Industry, VI (1934).

²P. B. Myers and G. L. Baker, Fruit Jellies VI The Role of Pectin, University of Delaware Agricultural Experiment Station Bulletin 160 (1929).

³L. W. Tarr, Fruit Jellies II The Role of Sugar, University of Delaware Agricultural Experiment Station Bulletin 136 (1924).

⁴E. G. Halliday and I. T. Noble, Food Chemistry and Cookery (Chicago: The University of Chicago Press, 1943), p. 92.

⁵Ibid.

Proof that the hydrogen ion concentration as such, and not the total acidity is the important factor is shown¹ by the fact that at a given pH value highly ionized inorganic acids will give the same results as naturally occurring weakly ionized acids. Tarr placed² the optimum value at 3.2 Ogg as cited by Norman³ found it to be 2.45 with limiting values of 2.1-2.7, outside of which no jelly is formed. This discrepancy may be due to the pectin used or to the presence of salts which do or do not facilitate gelation.⁴

Relative Viscosity of Extracts

The relative viscosity of a solution is at present used by Baker⁵ as a basis for the determination of the sugar holding capacity of an extract and the actual jelly yield. This is based on the finding that the relative viscosity of a solution seems to be a fairly good measure of the gelation value of the pectin present in the extract which is dependent on a combination of its quality and quantity. Baker claims that below a relative viscosity of 4.0 no jelly is obtained without the addition of pectin.

It must be observed that other factors, besides relative viscosity influence the sugar requirement of an extract for gelation. The sugar holding capacity of a solution will be affected by the acid as hydrogen ion concentration for with an increase in acidity, the amount of sugar which is required for gelation is decreased.

EXPERIMENTAL WORK WITH SYNTHETIC JELLIES

Reports in the literature seem to indicate that acid, pectin and sugar must be present in rather definite proportions if an excellent jelly is to be obtained. In order to determine if

¹L. W. Tarr, Fruit Jellies I The Role of Acids, University of Delaware Agricultural Experiment Station Bulletin 134 (1923).

²Ibid.

³Halliday and Noble, op. cit., p. 94.

⁴Ibid., p. 92.

⁵G. L. Baker, "How Much Sugar in Fruit Jellies," Food Industry, April, 1935, p. 170.

such quantitative relationship is required experimental work was carried on with synthetic jellies.

This work consisted of three parts. A so-called standard jelly was first prepared using sucrose, 0.1 normal tartaric acid, and citrus fruit pectin obtained from the California Fruit Grower's Association. This standard jelly was considered excellent in that it was decidedly quivery, held its angles when cut, and did not show syneresis or weeping.

Then the effect of varying the acid, sugar and pectin was observed by altering one of these factors gradually while maintaining the remaining two constant as in the standard. It was found that if any of the three factors essential for gelation are decreased from that proportion which results in an excellent jelly, in this case the standard, the product obtained will be too weak or no jelly at all. Increased sugar or pectin made the jelly too tough, while increased acid content caused little change within a rather wide limit, although it finally resulted in syneresis.

Another set of experiments with the synthetic solutions was carried out to find whether or not the deficient products obtained in the previous set could be made excellent by compensation of one factor by another. This time the deficient factor was maintained constant and one of the other two increased gradually. Thus to a syrupy product which contained less sugar than the standard was added first pectin and then acid. It was found as a result that in all cases save one, when a jelly was slightly deficient in any one factor increase of another compensated for the deficiency. The one exception was that increase in pectin alone did not compensate for a sugar deficiency even if the concentration of pectin was as high as 3 per cent.

In general all the experiments with synthetic jellies showed definitely that although there exists a quantitative relationship among the pectin, acid and sugar content of jellies no one definite proportion is required for gelation. Table 1 indicates eleven different proportions of exactly the same ingredients all of which produced excellent jellies.

TABLE 1

PECTIN, ACID, AND SUGAR CONTENT OF EXCELLENT
SYNTHETIC CITRUS FRUIT PECTIN JELLIES

No.	Sugar	Acid Content in Terms of Tartaric Acid		Pectin	Relative Viscosity Pectin Solution ^a	Jelly Strength ^b
		Extract	Jelly			
	per cent	per cent	pH	per cent		
1	65	0.104	2.34	0.50	4.3	10
2	60	0.104	2.34	0.50	4.3	11
3	57	0.052	2.54	0.75	9.5	33
4	55	0.052	2.54	1.13	13.0	17
5	55	0.052	2.54	1.25	18.0	23
6	55	0.104	2.45	0.75	9.5	21-26
7	55	0.156	2.27	0.75	9.5	21
8	55	0.208	2.16	0.75	9.5	21
9	55	0.261	2.11	0.75	9.5	21
10	55	0.313	1.98	0.50	4.3	19
11	50	0.417	1.91	0.50	4.3	17
12	50	0.417	1.91	0.75	9.5	11

^aPectin Solution contained 5 grams of sugar per 100 ml.

^bJelly Strength measured as centimeters of water pressure required to break the surface of the jelly.

EXPERIMENTAL WORK WITH FRUIT EXTRACTS

As has been stated, the purpose of the experimental work with fruit jellies was to determine if available formulae apply or can be made to apply in the preparation of excellent products of low sugar concentration from different fruits or different varieties of the same fruit.

This purpose was accomplished by preparing fruit extracts using various proportions of fruit to water, adjusting their pH value within the range of that suggested for gelation and preparing 50 and 55 per cent final sugar concentration jellies. These were prepared either by adding the amount of sugar calculated by use of the Baker formula based on the relative viscosity of an extract, or by using variations of the formula, by altering the

sugar added in several definite proportions. When the proportions of sugar to extract suggested by the formula were not satisfactory the variations used were based on the results of the experiments with synthetic jellies and provided compensation for a deficient factor by another factor.

In order to obtain a measure of the combination of the quantity and quality of the pectin in one extract as compared to others relative viscosity measurements were made and further evaluation of the quantity of the pectin was determined by carrying on calcium pectate determinations.

Fruits Analyzed

Guava and apples were the fruits included in this study. Guavas were the wild variety obtained from Florida; apples were the Cortland, Joan, Haralson, McIntosh, Hawkeye and Jonathan varieties obtained from Minnesota. All the apples analyzed were picked at the same time, and shipped under identical conditions to Chicago, where they were kept in storage until ready to be used. All the apple extracts were obtained within two weeks time after the arrival of the fruit. Guava extracts were obtained within three days after the arrival of fruit.

Preparation of Extracts

All extracts were prepared as follows: the fruit was washed and selected, then extractions were made by combining different proportions of fruit and water and boiling. Guava extracts were made by using from three to one parts of water per part of fruit. Apple extracts were prepared by using from one and one-half to one-half part of water to one part of fruit.

Only one extraction was made and at all times the mixture of fruit and water being used for an extraction was allowed to boil for 20 minutes. The extract was then drained in a jelly bag undisturbed for two hours. The extraction was heated to boiling, poured into jars and sterilized in a steamer for ten minutes, cooled and stored until ready to be used. The extracts were all made and stored at one time in order to prevent the fruit from standing varied periods of time and the quality of the pectin to be thus affected.

Quantitative Analysis of Extracts

In order to compare the products obtained as to composition, the following determinations were carried out in all extracts; hydrogen ion concentration expressed as pH, pectin content in terms of calcium pectate and relative viscosity.

Determination of hydrogen ion concentration.--The hydrogen ion concentration of each extract was determined electrometrically with the use of a Leeds and Northrop glass electrode apparatus and expressed as the pH of the solution. If the pH of the solution was above the limiting values expressed by previous workers,¹ 2.1 to 3.2, the same was adjusted by the addition of tartaric acid crystals.

Although the original extracts varied from a pH value of approximately 3.0 in apple extracts to over 6.00 in the case of the guava extracts the results in Table 2 indicate that the final pH of the extracts used ranged from 2.58 to 5.00.

TABLE 2

SUMMARY OF FRUIT EXTRACTS ANALYZED AND JELLIES PREPARED

Fruit	Number of Extracts Analyzed	Total Number of Jellies Prepared ^a	pH Range	Relative Viscosity Range	Jelly Strength Range ^b
Guava	20	127	2.58-5.00	3.9-10.0	3-64
Apples					
Jonathan	20	62	2.98-3.16	2.7-7.7	10-86
Cortland	12	51	2.99-3.20	3.0-7.1	10-87
Hawkeye	14	59	2.80-3.14	2.1-8.7	9-100
McIntosh	14	69	2.80-3.10	4.4-7.5	3-40
Haralson	16	29	2.80-3.15	2.5-5.1	18-88
Joan	16	60	2.83-3.20	3.1-7.8	8-49

^aTwo to six jellies of 50 to 55 per cent sugar concentration from each extract prepared. Number depending on the number of variations of Baker's formula used.

^bJelly strength expressed as cm. of water pressure required to break the surface of the jellies. Each value is an average of three determinations which varied no more than 3 units from the average.

¹Halliday and Noble, op. cit., p. 109.

TABLE 3
SUMMARY TABLE OF EXCELLENT JELLIES OBTAINED
WITH FRUIT EXTRACTS^a

Fruit	Total Number of Excellent Jellies Prepared	pH Range of Extracts	Relative Viscosity Range of Extracts Used	Jelly Strength Range of Products ^b	Selected Fraction of the Calculated Sugar Added per Part of Extract Ac- cording to Baker's Formula	
					First Choice	Second Choice
Guava	35	2.58-3.52	3.9-8.7	6-38	0.750	0.875
Apples						
Jonathan	33	3.06-3.16	3.8-7.9	29-74	0.875	1.000
Cortland	18	2.99-3.20	3.1-7.4	25-74	0.875	1.000
Hawkeye	14	2.68-3.14	3.4-8.7	22-71	0.875	0.750
McIntosh	17	2.70-3.00	4.4-7.5	11-36	0.875	0.750
Haralson	16	2.80-3.15	3.5-5.5	57-79	1.000	0.875
Joan	16	2.96-3.20	5.1-6.3	21-41	0.875	1.000

^aIncludes all those selected as first choice and several second choice, whose lower rating was due to a slight difference in preference of flavor.

^bJelly Strength expressed as centimeters of water pressure required to break the surface of the jelly. Each value is an average of three determinations which varied no more than three units from the average.

Determination of pectin.--Preliminary determinations of pectin as calcium pectate were done on several extracts using the alcohol method, the calcium pectate method and the combination alcohol-calcium pectate method according to Simpson.¹ The alcohol method gave the highest results due to impurities brought down by the alcohol; the second highest were obtained by the calcium pectate method, and the lowest by the combination methods as indicated in Table 4.

¹J. I. Simpson and E. G. Halliday, "Chemical and Histological Study of the Disintegration of Cell Membrane," Food Research, VI (1941), 189-206.

TABLE 4

THE PECTIN CONTENT OF THREE APPLE EXTRACTIONS
OBTAINED BY DIFFERENT METHODS

Extraction	Pectin		
	Alcohol Method	Calcium Pectate Method	Combination Method
	per cent	per cent	per cent
a.....	0.79	0.43	0.39
b.....	0.40	0.31	0.23
c.....	0.45	0.30	0.19

As the results corresponded with those obtained by other workers¹ only the calcium pectate combination method was used in determining pectin content of all extracts. The procedure for the determination follows.

To 150 ml. of a 95 per cent ethyl alcohol in a 250 ml. beaker were added 15-20 drops of concentrated hydrochloric acid (making an approximately tenth normal solution). To this was added from a burette, a known amount of fruit extract, stirring during the addition. This alcohol-fruit extract solution was allowed to stand at least several hours (usually overnight), then it was filtered through folded filter paper. The gel remaining on the filtered paper was washed with acidified 70 per cent alcohol.

When the washing was completed, the beaker receiving the alcohol washings was replaced by a clean one to receive the pectin, and hot water was added to the gel on the filter paper. Most of the gel dissolved readily passed through the filter paper into the beaker, and any small particles of gel sticking to the paper were removed with a small spatula and added to the solution. They were readily dissolved by the addition of a drop or two of concentrated ammonium hydroxide.

To the solution of pectin obtained in this manner, 40 ml. of tenth normal sodium hydroxide were added and the solution was allowed to stand at least several hours (usually overnight). The

¹Ibid.

following morning, 25 ml. of normal acetic acid were added and after five minutes 25 ml. of molar calcium chloride (with stirring) to precipitate the calcium pectate. The solution was then allowed to stand several hours but usually overnight, to insure complete precipitation of the calcium pectate.

The solution containing the calcium pectate gel was boiled for five minutes, to dissolve as much as possible of the chlorides present, then it was filtered through hardened filter paper in a Buchner funnel. The calcium pectate jelly obtained was washed with 800-1,000 ml. boiling distilled water or until the washings were free from chlorides when tested with silver nitrate. At this point the jelly was transferred to a small beaker 25-59 ml. of water were added and the solution was boiled for several minutes to dissolve any remaining chlorides. The solution was again filtered and the jelly was washed as before until free from chlorides. This procedure of reboiling and retesting was repeated until the first washings after boiling were found to be free from chlorides.

The gel was then transferred to a small weighing bottle previously dried to constant weight at 100° C., and the filter paper was rinsed with a small amount of boiling water adding the rinsings to the weighing bottle. The calcium pectate was then dried to constant weight at 100° C.--which usually required about twelve hours.

On each extraction solution four quantitative extractions of pectin were made by this method, and the following is a typical set of four weights of calcium pectate resulting.

0.0236 gram of calcium pectate
0.0243 gram of calcium pectate
0.0240 gram of calcium pectate
0.0235 gram of calcium pectate

The average of the four weights is 0.0239 gram of calcium pectate.

In Table 5 are reported the calcium pectate yields of several representative samples of guava and apple extracts expressed in terms of per cent extract. The third and fourth extracts of the Cortland apple in Table 5 indicate two separate calcium pectate determinations on the same extract as a sample of how different determinations carried on the same sample would correlate.

All the data in Table 5 clearly indicate that relative viscosity definitely increased with an increase in the calcium pectate content of the fruit extract and therefore, is a measure

TABLE 5
RELATIVE VISCOSITY AND CALCIUM PECTATE
YIELD^a OF FRUIT EXTRACTS

Fruit Extract ^b		Relative Viscosity	Calcium Pectate
I Guava			per cent
	1	4.8	0.190
	2	5.5	0.233
	3	5.7	0.259
	4	5.8	0.276
	5	6.3	0.281
	6	7.3	0.318
II Apple			
Jonathan	1	2.7	0.110
	2	3.8	0.147
	3	4.4	0.162
	4	7.1	0.265
	5	7.9	0.272
Cortland			
	1	3.0	0.147
	2	3.3	0.164
	3	3.7	0.187
	4	3.7	0.188
	5	3.8	0.193
Hawkeye			
	1	2.1	0.078
	2	3.1	0.166
	3	4.4	0.192
	4	7.7	0.312
	5	8.7	0.316
McIntosh			
	1	4.4	0.113
	2	4.8	0.123
	3	5.7	0.160
	4	6.9	0.182
Haralson			
	1	2.3	0.075
	2	2.5	0.076
	3	4.0	0.159
Joan			
	1	5.1	0.200
	2	5.2	0.203
	3	5.7	0.214
	4	5.9	0.215

^aExpressed as per cent of fruit extract computed from the average of four weights of calcium pectate in each case.

^bDifferent fruit extracts obtained by varying the proportion of fruit to water used in the original extraction.

of the quantity of the pectin present. However, same data clearly show that it is not merely a quantitative measure but a qualitative measure as well for the extracts of different varieties of fruit having the same relative viscosity did not have the same calcium pectate content. This is clearly shown by comparing the Guava, McIntosh apple and Joan apple extracts which had identical relative viscosity of 5.7 and yet their calcium pectate content expressed as per cent of extract was 0.259, 0.160 and 0.124 respectively, as indicated in Table 5.

Preparation of Jellies

In making all jellies the following standard procedure was followed: First the hydrogen ion concentration of the extract was determined in terms of pH value. If it was outside of the range of 2.8 to 3.2 it was adjusted to fall within that range. The exceptions were the guava extracts which ranged from 2.58 to 5.0 as will be discussed in the results.

Once the hydrogen ion concentration was adjusted, the relative viscosity of the extract was determined using the Baker-Ostwald viscosity pipette and the amount of sugar to be added per part of extract calculated according to the Baker jelly formula.¹

This formula, used for the determination of the sugar holding capacity of a juice and based on the relative viscosity of the extract is as follows:

$$\log y = ax + b$$

in which the viscosity is represented by y ; a and b are two determined constants, .675 and .236 respectively; and x stands for the amount of sugar to be added per part of extract. Using this same relation the actual yield of jelly is determined. In this case the same constants a and b are kept and the variables c and z introduced. The first represents the concentration of added sugar in the final product and the latter the jelly yield. The formula thus obtained is $\log y = acz + b$.

If the jellies prepared by using the formula as presented resulted in excellent products then it was unquestionable that the formula could be applied successfully for the particular fruits being used and no further work needed to be done.

¹Halliday and Noble, op. cit., p. 109.

Previous experiments undertaken, however had indicated that the Baker's viscosity formula did not work satisfactorily for synthetic or youngberry jellies of only 55 per cent sugar concentration. If the results of the actual experimental work agreed with the preliminary experiments and the jellies were too soft, another proportion or adaptation of the formula was tested.

As shown by previous work with synthetic solutions a slight deficiency of any one factor required for gelation could be compensated by a slight increase in another factor. Therefore if an increase in the proportion of extract to sugar were tried, it would provide a greater quantity of pectin and acid per part of the final jelly when the final sugar concentration was kept constant. Just how much alteration of the proportion of sugar to extract should be made was indefinite, therefore some preliminary work was undertaken and three different proportions finally selected. These are essentially as follows:

Proportion 1. Jellies prepared according to the Baker viscosity formula with a final sugar concentration of 55 or 50 per cent.

Proportion 2. Jellies whose final sugar concentration was 55 per cent or 50 per cent just like in those of the proportion above mentioned but in which only 87.5 per cent (or seven-eighths) of the calculated amount of sugar per part of extract was used. For example, if jellies were to be prepared from an extract with a relative viscosity of 7.5, then according to the Baker formula 0.95 part of sugar per part of extract was to be used, and the mixture boiled down to a final weight of 1.72 per part of extract used. Instead, only 0.83 part of sugar per part of extract was used, and the extract-sugar solution boiled down to 1.51 per part of extract used.

Proportion 3. Jellies whose final sugar concentration was 55 or 50 per cent were prepared just like in those of the sets just mentioned but only 75 per cent (or three-fourths) of the calculated amount of sugar per part of extract was used.

Thus it is evident that the products prepared by the two modifications of the Baker viscosity formula, due to the fact that they had a smaller proportion of sugar to juice, had a greater concentration of pectin and acid in the final jelly, although an identical final sugar concentration.

In order to determine which of the three proportions gave

the most satisfactory results with each extract it was necessary that several jellies be prepared from the extract and the products obtained compared. The following is a list of the different jellies which were prepared from one extract.

1. A jelly using the formula suggested by Baker and a final sugar concentration of 55 per cent.
2. A jelly using the formula suggested by Baker and a final sugar concentration of 50 per cent.
3. A jelly using 87.5 per cent of the calculated amount of sugar per part of extract calculated by the formula, but boiled down to a final sugar concentration of 55 per cent.
4. A jelly using 87.5 per cent of the calculated sugar per part of extract but boiled down to a final sugar concentration of 50 per cent.
5. A jelly using 75 per cent of the calculated amount of sugar per part of extract and boiled down to a final sugar concentration of 55 per cent.
6. A jelly using 75 per cent of the calculated amount of sugar per part of extract and boiled down to a final sugar concentration of 50 per cent.

Boiling down the solution¹ to the calculated final weight was accomplished by placing the jelly ensemble (beaker which was to contain the mixture, a tripod, wire gauze and burner) on the left hand side of a torsion balance, and its counterpoise on the right side. The sugar-extract solution was then poured into the beaker, the weight in grams equivalent to the calculated final weight of the solution placed on the right side of the balance, and the solution boiled until the pointer came to a balance.

Once the jelly was concentrated to the determined weight it was poured into 100 ml. beakers and placed in the refrigerator along with the remaining samples of the set. All the jellies of a given extract were prepared within a two hour period and allowed to stand for forty-eight hours. They were then judged by various objective and subjective tests.

Objective Test

Jelly strength in terms of the force required to break the surface of the jelly was the objective test used. This was carried out in all the jellies using an apparatus designed at the Delaware Agricultural Experiment Station, University of Delaware,

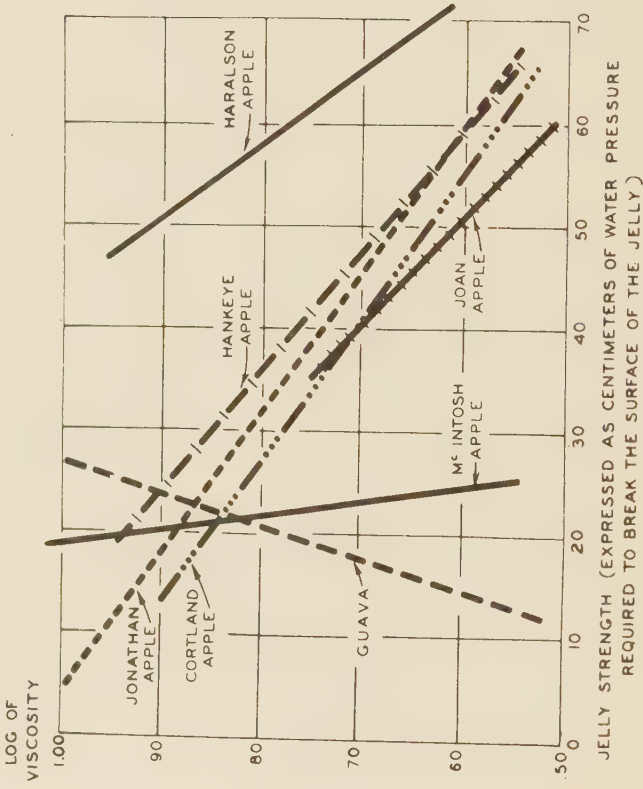
¹Halliday and Noble, *op. cit.*, p. 113.

and described by Baker.¹ The process involved is as follows: Mercury is dropped from a reservoir which creates air pressure in a receiving flask. This pressure is then distributed evenly into a manometer and a T-glass tube. The latter is connected with a Luer syringe which has the plunger placed over the surface of the jelly. The pressure exerted is allowed to increase until the plunger breaks the surface of the jelly. The reading on the scale which corresponds to the highest peak reached just before descent, was taken as a measurement of the jelly strength. It was recorded in terms of centimeters of water pressure required to break through the jelly. All measurements were made on the bottom of the jelly after it was removed from the beaker. No measurement was done on the top of the jelly due to the fact that a hard skin effect caused at times a high reading. The results of the jelly strength measurements indicated that there is not a perfect correlation between the relative viscosity of an extract and the jelly strength of its jellies, for such factors as the pH value of the extract influence the strength of the jellies. For example if Guava extracts numbers 3 and 4 or 11 and 12 in Table 7 are compared it will be observed that although their relative viscosity is the same or approximately the same, the extracts having the lower pH value gave much stronger jellies or jellies of a higher jelly strength than those prepared from the extract of higher pH value.

Figure 1 indicates the relationship between the relative viscosity of apple and guava extracts and the strength of the jellies obtained. This was calculated from data on the jellies which were considered first or second choice. Variations from the line were approximately plus or minus 6 jelly units. The results graphed in this figure indicate that in all apples except McIntosh, there was a marked tendency to form jellies of higher strength as the relative viscosity of the extracts used decreased. This was not true in the case of the guava or McIntosh apple. For guava there was in fact a slight trend in the opposite direction.

Low relative viscosity extracts have to be concentrated more than those of a high viscosity since less sugar has been added per part of extract. This resulted in a longer boiling

¹G. L. Baker, "Jelly Strength Measurement," Fruit Products Journal, XVII (1938), 329-30.



THE RELATIVE VISCOSITY OF APPLE AND GUAVA EXTRACTS
AND THE STRENGTH OF JELLIES PRODUCED

FIGURE 1

period. If it were assumed that the strengths of apple pectins were not greatly affected even with the long heating periods involved, the higher final concentration of pectin in the jellies from lower viscosity extracts could be one of the factors bringing about stronger jellies. It is the only one of the several factors possibly concerned, regarding which quantitative data were obtained. Final pectin concentrations for a representative number of jellies in each series are presented in Table 6, and they indicate that for jellies from apple extracts a slightly but fairly consistently greater concentration of pectin is obtained the lower the viscosity of the extract from which they were made. The only exception was the McIntosh apple. Guava and McIntosh jellies on the other hand had a trend to slightly lower calcium pectate when made from extracts of lower viscosity.

TABLE 6
CALCIUM PECTATE CONTENT IN JELLIES PREPARED FROM
EXTRACTS OF VARYING RELATIVE VISCOSITIES

Fruit	Relative Viscosity	Calcium Pectate in 100 Grams Extract	Weight of Jelly Obtained from 100 Grams Extract	Calcium Pectate Content per Gram Jelly
		mgs.	gms.	mgs.
Guava				
1	4.4	1.82	83	2.1
2	4.8	1.90	90	2.1
3	5.1	2.17	96	2.1
4	5.5	2.33	100	2.2
5	5.5	2.33	100	2.3
6	5.8	2.76	105	2.4
7	6.3	2.81	112	2.5
8	7.3	3.18	127	2.5
9	8.6	3.29	141	2.3
Apples				
Jonathan				
1	3.8	1.47	86	1.7
2	3.8	1.47	76	1.9
3	4.1	1.81	94	1.9
4	4.4	1.62	96	1.6
5	7.1	2.65	144	1.7
6	7.9	2.72	154	1.4
Cortland				
1	3.7	1.87	83	2.2
2	3.8	1.93	84	2.3
3	4.4	1.92	96	2.0
4	6.1	2.45	129	1.9
5	7.3	2.51	147	1.7
6	7.8	3.16	183	1.7

TABLE 6--Continued

Fruit	Relative Viscosity	Calcium Pectate in 100 Grams Extract	Weight of Jelly Obtained from 100 Grams Extract	Calcium Pectate Content per Gram Jelly
		mgs.	gms.	mgs.
Hawkeye				
1	4.4	1.92	97	2.0
2	4.7	2.18	104	2.0
3	7.7	3.12	153	2.0
4	8.7	3.16	179	1.8
Haralson				
1	4.0	1.59	93	1.7
2	4.7	1.87	107	1.7
3	5.1	1.88	116	1.6
4	5.5	1.98	124	1.6
Joan				
1	5.1	2.00	111	1.8
2	5.2	2.03	112	1.8
3	5.7	2.14	122	1.7
4	5.9	2.15	125	1.7
5	6.3	2.27	131	1.7
6	6.5	2.29	134	1.7
McIntosh				
1	4.4	1.13	96	1.1
2	4.7	1.19	100	1.1
3	4.8	1.23	105	1.1
4	5.3	1.44	114	1.2
5	5.7	1.60	122	1.3
6	6.9	1.82	140	1.3

This fact is in keeping with the difference between the line obtained from apples and from guava. It should be emphasized that these relationships are thus explained only on the assumptions that the differences in final pectin concentration are significant amounts and that no depolymerization or weakening of any of the pectins occurs during the longer boiling period of the lower viscosity extracts. However still other factors such as possibly greater final concentration of fruit acids and minerals in the jellies produced from the originally more dilute extracts need also to be reckoned with. If there were depolymerization of pectin such factors might counteract its effect. The jelly strength measurements of jellies obtained are proof of the fact that there

is a decided difference in the gelation properties of the extracts prepared from different fruits or even different varieties of the same fruit.

Subjective Tests

The jellies were also compared for texture and appearance and classified as to clearness, color and flavor, described by one of several adjectives. The adjectives suggested for the description of each characteristic were:

1. Firmness
 - no jelly
 - jelly but collapsed at once
 - soft jelly
 - good jelly but slightly soft, tough,
 - sticky or weepy
 - firm jelly
 - too tough, sticky or weepy
2. Clearness
 - clear
 - slightly cloudy
 - cloudy
3. Color
 - attractive
 - light
 - too light
4. Flavor
 - excellent
 - slightly sweet
 - slightly sour
 - too sweet
 - too sour

A group of judges was selected to compare each set of jellies. The jellies were arranged at random upon a table, and numbered. The judges were then asked to describe them and to grade them in the order of preference. Good correlation was obtained among the judges and the greatest difference was observed in the degree of acidity or tartness which was preferred. The following is a sample of the scoring of 5 jellies by one judge.

Jelly number	1	2	3	4	5
Firmness	firm	soft	firm	soft	soft
Clearness	clear	clear	cloudy	clear	clear
Color	attractive	light	too light	too light	light
Flavor	excellent	too sweet	too sour	too sweet	slightly sweet
Order of preference	1	4	5	2	3

TABLE 7

COMPOSITION AND STRENGTH OF SEVERAL OF THE JELLIES SELECTED
AS FIRST CHOICE BY SUBJECTIVE TESTING^a

Fruit Extract Sample ^b	pH	Relative Viscosity	Sugar Added		Final Sugar Concen- tration	Jelly Strength ^d
			Fraction of Baker's Formula	Parts per Part of Extract		
Guava					per cent	
1	2.74	3.9	0.875	0.43	55	14
2	2.92	4.4	0.750	0.46	55	21
3	2.84	4.6	0.750	0.47	55	16
4	2.58	4.6	1.000	0.63	55	38
5	3.14	4.8	0.750	0.50	55	6
6	3.04	5.5	0.750	0.55	55	8
7	3.04	5.5	0.875	0.65	55	15
8	3.20	5.8	0.750	0.58	55	15
9	2.78	6.3	0.750	0.62	55	10
10	3.00	7.3	0.750	0.70	55	28
11	3.52	8.6	0.750	0.79	55	28
12	2.99	8.7	0.875	0.92	55	26
Apple Jonathan ^{1c}						
1	3.12	3.8	1.000	0.49	55	59
2	3.12	3.8	0.875	0.42	55	74
3	3.14	4.4	0.875	0.53	55	72
4	3.06	4.6	0.875	0.55	55	49
5	3.08	7.1	0.875	0.79	55	59
6	3.08	7.9	0.875	0.86	55	51
7	3.08	7.1	0.750	0.68	55	42
Cortland						
1	3.09	3.1	1.000	0.23	55	74
2	3.20	3.3	0.875	0.24	55	25
3	3.16	3.8	0.875	0.46	55	62
4	3.09	3.7	0.875	0.47	55	64
5	2.99	3.7	0.875	0.47	55	46
6	3.19	4.1	0.875	0.51	55	53
Hawkeye						
1	2.98	3.4	1.000	0.47	55	71
2	3.08	4.7	1.000	0.65	55	45
3	2.97	4.4	0.875	0.53	55	42
4	2.89	7.7	0.875	0.84	55	39
5	3.14	8.7	0.875	0.92	55	32

TABLE 7--Continued

Fruit Extract Sample	pH	Relative Viscosity	Sugar Added		Final Sugar Concen- tration	Jelly Strength	
			Fraction of Baker's Formula	Parts per Part of Extract			
per cent							
Apple McIntosh	1	3.00	4.4	0.875	0.54	55	23
	2	2.83	5.7	0.875	0.67	55	24
	3	3.00	6.9	0.875	0.77	55	25
	4	2.73	7.5	0.750	0.71	55	23
	5	2.81	4.8	0.875	0.58	50	20
	6	2.80	6.7	0.875	0.76	50	21
	7	2.91	5.3	0.875	0.63	50	11
Haralson	1 ^c	3.15	3.5	1.000	0.47	55	70
	2	3.00	4.0	1.000	0.51	55	57
	3	3.00	4.7	0.875	0.57	55	74
	4	3.00	4.7	1.000	0.65	55	57
Joan	1	3.20	5.1	0.875	0.61	55	41
	2	3.20	5.7	0.875	0.67	55	27
	3 ^c	3.05	5.9	0.875	0.69	55	37
	4	3.05	5.9	1.000	0.79	55	21

^aIn each case the selection was made from four to six jellies prepared from the same extract but varying in proportion of sugar added per part of extract used.

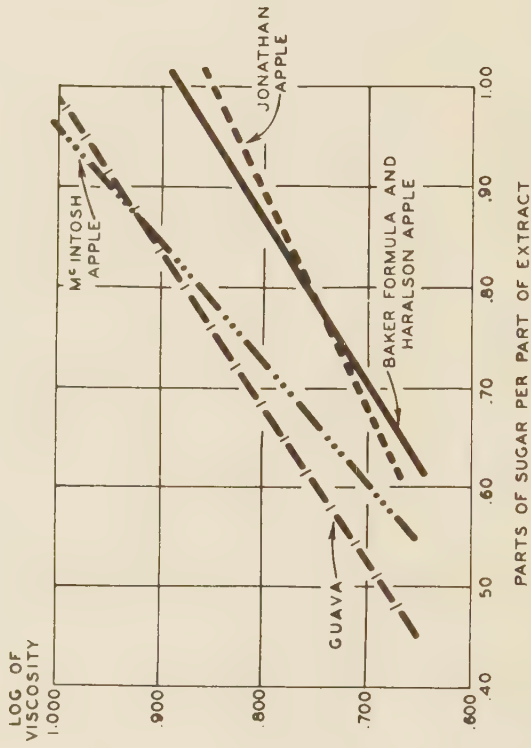
^bOf the total number of jellies of each fruit selected as first choice (Table 3) those presented in this table were considered to represent all variations in pH and relative viscosity, and to present extremes as well as average jelly strength measurements.

^cSelected as second choice because of flavor. Otherwise as good as first choice.

^dJelly Strength expressed as centimeters of water pressure required to break the surface of the jelly. Each value is an average of three to five determinations which varied no more than three units from the average.

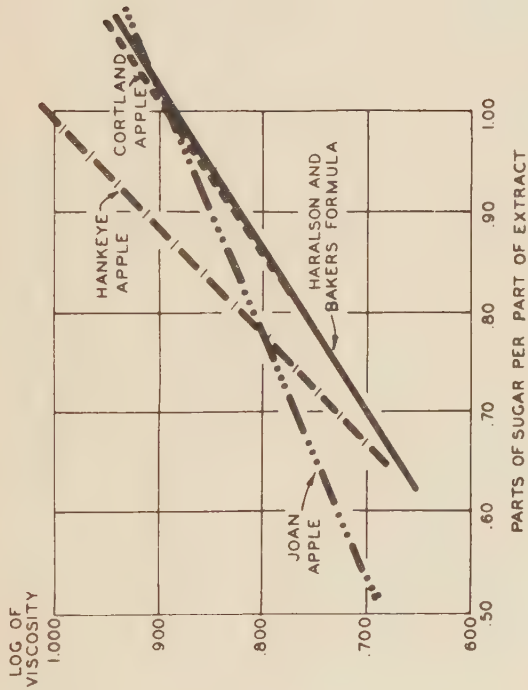
Sugar Holding Capacity of Extracts

As graphed in Figures 2 and 3, the sugar holding capacity of the extracts analyzed showed a straight line relationship to the logarithms of their viscosities, similar to that given by



SUGAR REQUIREMENT OF APPLE AND GUAVA EXTRACTS COMPARED
TO VALUES CALCULATED FROM BAKER'S FORMULA

FIGURE 2



SUGAR REQUIREMENT OF APPLE EXTRACTS COMPARED
TO VALUES CALCULATED FROM BAKER'S FORMULA

FIGURE 3

Baker's formula for lemon albedo pectin. The equation calculated for each fruit by the method of least squares gave the following values for the constants a and b in the formula:

$$\log y = ax + b$$

Guava	$\log y = .737 x + .305$
Apples	
Jonathan	$\log y = .311 x + .468$
Cortland	$\log y = .550 x + .309$
Hawkeye	$\log y = .079 x + .939$
McIntosh	$\log y = .213 x + .820$
Haralson	$\log y = .675 x + .236$
Joan	$\log y = .251 x + .586$
Baker's formula	$\log y = .675 x + .236$

For each fruit these calculations included data from all jellies considered first choice and a few of those selected as second choice, when the lower rating was mainly due to a slightly less desirable flavor. As Figures 2 and 3 indicate the sugar holding capacities of the fruits analyzed were as a whole lower in relation to their viscosities than that indicated by Baker's formula. Haralson apple extracts, however, agreed with Baker's proportions since those jellies selected as first choice were the ones prepared by using the formula. Jonathan and Cortland apples have a similar sugar holding capacity to Haralson although this is not so apparent from the values of their a and b constants in the equation. The lowest sugar holding capacities and the greater variations from Baker's formula were shown by the guava and McIntosh apple extracts. These findings are in agreement with the weaker properties of guava pectins and the lower concentration of pectins in relation to viscosity in McIntosh extracts, and lead to weaker jellies in these series.

Summary of Results of Experimental Work with Fruit Extracts

The results obtained clearly indicate that the relative viscosity measurements of a fruit extract is a measure of both the quality as well as the quantity of the pectin present. This was indicated by the fact that the extracts prepared from different varieties of apples and from guava and which had the same relative viscosity measurement did not have the same calcium pec-

tate content. Surprisingly enough the guava and Joan extracts which had the highest pectin content for the same relative viscosity measurement, gave weaker jellies than those prepared from extracts of other varieties of apples, which had a lower calcium pectate content. Therefore the guava and Joan apple extracts appeared to have a greater quantity of pectin but of poorer quality.

Extracts of a relative viscosity of 4.0 or below did produce excellent jellies of 55 per cent final sugar concentration. This is not in agreement with present belief that excellent jellies cannot be obtained from extracts of a relative viscosity below 4.0 unless pectin is added.

Excellent jellies were obtained at a much wider range of pH than ever has been reported by other workers. This was indicated by the guava extracts which gave excellent jellies within a range of 2.58 to 3.52.

There was a great difference between the gelation properties of guava and apple extracts as indicated by the products obtained through the use of suggested formulas or their modifications. These differences may be summarized as follows:

1. Relative viscosity of extracts:

Guava extracts had a much higher relative viscosity than those prepared from apples by using the same proportion of fruit to water. That is to say if a guava extract prepared from one part of fruit to one part of water had a relative viscosity of 8.0, the same proportion of fruit to water gave with a certain variety of apples an extract of only 5.0 viscosity.

2. Calcium Pectate Content and Relative Viscosity compared:

Two extracts of the same relative viscosity usually gave a higher calcium pectate content for the guava extract than for the apple extract. Guava extracts had a greater quantity of pectin as calcium pectate.

3. Jelly Strength:

Weak jellies or products of low jelly strength were obtained at all times from guava extracts. Those from apples were usually much stronger. The only exception was the McIntosh apple which at times gave jellies almost as weak as those from guava. The higher the relative viscosity of the guava extracts, the greater the jelly strength of the jellies.

4. Comparison of jellies obtained with a final sugar concentration of 55 per cent:

No guava jelly was obtained when Baker's formula was applied. The only exception was an extract with a pH of 2.58. The formula did apply

successfully to five of the six varieties of apples.

In nearly all cases guava jellies prepared by using only 87.5 per cent of calculated sugar per part of extract were too soft. The best products with this proportion were obtained with guavas when extracts of low relative viscosity and low pH value were used. All varieties of apples gave excellent products with this modification of the formula. It actually resulted in the jellies considered as first choice for five of the six varieties of apples.

Guava jellies prepared with 75 per cent of the calculated sugar per part of extract were those considered excellent. Guava therefore required a much greater concentration of extract in the final jelly than did any of the apples. Only McIntosh, Jonathan and Hawkeye apples gave excellent products with this modification. Jellies obtained with the other three varieties of apples were too firm or too sour.

5. Comparison of jellies with 50 per cent final sugar concentration:

Excellent 50 per cent final sugar concentration products were obtained from guava extracts when the modification of 75 per cent of the calculated sugar per part of extract was used. All apples resulted in excellent 50 per cent sugar jellies when the proportion of sugar to extract used was 87.5 per cent of that calculated by formula.

6. Sugar Holding capacity of extracts:

Guava extracts had a lower sugar holding capacity than apples. McIntosh apple, which had the lowest sugar holding capacity of the apples, was the most similar to guava.

In view of these results, it is concluded that guava jellies cannot be prepared by using the Baker formula. Experimental results indicate that if a modification is used so that only 75 per cent of the calculated sugar per part of extract is added, excellent products can be assured. Such excellent products were obtained within a range of 2.58 to 3.52 pH. Results likewise clearly indicate that guava extracts have a greater quantity of pectin but of lower gelation properties than those from apples. Although a much greater difference was observed between the gelation of apples and guava, variation within the six varieties of apples were most significant. These differences may be summarized as follows:

1. Relative viscosity and calcium pectate content:

Jonathan, Cortland, Hawkeye and Haralson apples gave similar values of calcium pectate content for a corresponding relative viscosity.

Joan apples gave higher calcium pectate content for extracts of the same relative viscosity.

2. Jelly strength of jellies from different varieties of apples:

Jonathan, Cortland, Haralson jellies were of greater jelly strength than Joan and McIntosh. Weakest jellies were obtained with the McIntosh apples; with which never a tough jelly was produced. Strongest products were from Haralson apple. Appearance and jelly strength measurement did not correlate. For example Jonathan jellies must be described as appearing to be softer than they tested; Cortland and Joan jellies appeared to be stronger than they tested. It must be observed that jelly strength within the same variety of fruit varied with the proportion of sugar to extract used, and with the pH value of the extract.

3. Comparison of 55 per cent sugar concentration jellies:

The best products obtained from Jonathan, Cortland, Hawkeye, Joan and McIntosh apples were those where only 87.5 per cent of the calculated sugar per part of extract was used. With Haralson apple the best products were those obtained by using the Baker formula.

Second choice for Jonathan, Cortland and Joan jellies were those prepared according to the Baker formula. Haralson apple jellies considered second choice were usually those prepared by the 87.5 per cent modification. This proportion at times resulted in too firm products. Second choice for the McIntosh and Hawkeye apples were those prepared by using 75 per cent of the calculated sugar per part of extract. The Baker formula did not work for the McIntosh and Hawkeye apples, for the products obtained were always too soft. Of the six varieties of apples, Jonathan apples were considered to have the best gelation properties. It was likewise the variety with which all the three proportions of sugar to extract resulted in excellent products.

4. Jellies prepared with 50 per cent final sugar concentration:

All the varieties of apples produced excellent 50 per cent sugar concentration jellies if the proportion of 87.5 per cent of calculated sugar per part of extract was used.

Conclusions

The results obtained in the experimental work with fruit jellies substantiate previously established relationships among pectin, acid and sugar in the gelation of extracts. These are:

1. Relative viscosity is a measure of both quantity and quality of pectin in an extract.

2. At lower pH value the sugar holding capacity of an extract is increased.
3. Slight deficiency of one factor essential for gelation may be compensated by a slight increase in one or more of the other factors.

Although a quantitative relationship does appear to be essential for the gelation of a particular extract under a definite set of conditions, there is no one definite quantitative proportion of pectin, acid and sugar required for gelation. Excellent jellies can be obtained within a most varied concentration of these three factors as indicated both by synthetic and fruit jellies experiments.

The results likewise indicate that there is a considerable variation in the gelation properties of different fruits and even of different varieties of the same fruit. Therefore one formula is not satisfactory for assuring excellent products at all times, or products of a definite jelly strength. A variation of the Baker-viscosity formula so that only 87.5 per cent of the calculated sugar per part of extract was used, worked satisfactorily for five out of six varieties of apples. Only when 75 per cent of the calculated sugar per part of extract was used, were excellent guava jellies obtained. Adaptation must therefore be made of formulas according to the type of fruit and even according to the variety of the fruit.

Jelly strength of jellies prepared with identical final sugar concentration varies according to the pH of the extract, its relative viscosity, type of fruit and even variety of fruit used.

STRUCTURE OF PECTIN GELS

Norman¹ suggests that pectin is precipitated in the form of a network of threads or fibrils with sugar solution in the interstices. Schneider and Bock² claim that such a network exists

¹R. R. Dastur and S. D. Agnihorti, "Study of the Pectic Changes in Potato Tubers at Different Stages of Growth," Indian Journal of Agricultural Science, IV (1934), 430.

²G. G. Schneider and H. Bock, "The Constitution of Pectic Substances," Berichte, LXX (1937), 1617.

in pectin gels and that it is visible under the ultra microscope. Previous experimental work with synthetic jellies and fruit extracts had indicated a possible change of structure of jellies as the solution was disturbed while settling.

As a result attempts were made to study the structure of gels if any such structure did exist. This was to have been the main part of the experiment if the investigations had proved successful.

Use of Dark Field Microscope

Attempts were first made to use a dark field microscope for the determination of pectin structure in gels. In case the structure was large enough to be seen with this type of instrument. No structure could be observed.

Slit-Ultramicroscope

The dark field microscope deals with relatively larger particles, that is those within the revolving power of the microscope, yet the ultra microscope deals with objects so small that they do not even show as objects, but one infers their presence by the points of light which they turn. Attempts were therefore made to use the latter type of microscope, in the study of the structure of gels.

The apparatus used was a slit-ultramicroscope available in the chemistry department of the University of Chicago. A special cell was constructed to resist the high temperature of the jellies when removed from the flame. Once the solution was boiled down to the desired final sugar concentration it was immediately poured into the microscope cell and allowed to set undisturbed so that the structure of the jelly would not be altered.

Numberless attempts were made to measure or observe any network structure in the pectin gel, but all proved unsuccessful. This does not imply that a structure does not exist but it probably indicates that the particles were too small to be distinguished with the apparatus available.

RELATIONSHIP AMONG THE PHYSICAL AND CHEMICAL PROPERTIES OF FRUIT PECTINS

Experimental work with the fruit extracts prepared from guava and six varieties of apples had indicated that there exists a wide variation in the gelation properties of extracts from the different fruits and even among the six varieties of the same fruit. For example guava products were much weaker than those obtained from any of the apple extracts. Attempts were therefore then made to determine any possible relationship between the chemical properties of the pectins and their gelation behavior.

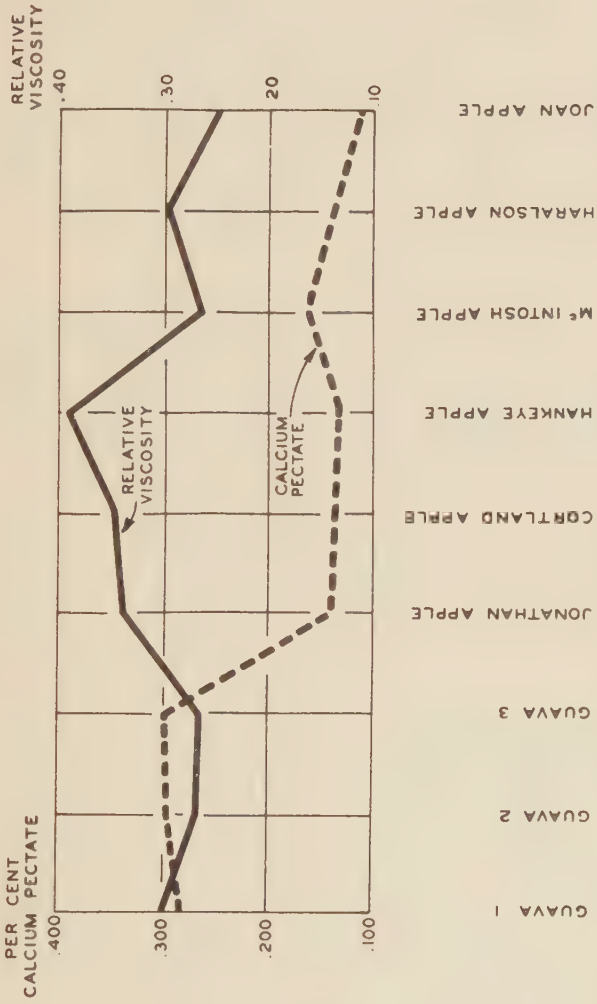
With this purpose in mind pectins were extracted from the same lots of guavas and from the six varieties of apples used for preparation of jellies, and their chemical properties determined.

Extraction of Pectins

Preliminary work was carried out following different suggested methods for the extractions of pectin from fruits. The method which proved most satisfactory within the prevailing laboratory conditions was one of those suggested by Hinton,¹ which is essentially as follows.

The fruit was finely chopped and immediately poured into water at 80° C. and placed over a water bath. The temperature of the fruit extract was kept constant at 80° C. for one hour. The fruit and water mixture was then removed from the steam bath and allowed to cool for another hour. The mixture was then immediately pressed with a fruit press. To the extract obtained was added 50 per cent acetone and the pectin precipitated. The pectin was then filtered off, redissolved by warm water at 50° C. or below and the solution passed through a centrifuge. The pectin solution thus obtained was then once more precipitated with acetone up to 50 per cent with a little sodium chloride added to assist coagulation. The pectin was then soaked in several changes of 98 per cent acetone and finally allowed to dry in a desiccator at ordinary temperature.

¹C. L. Hinton, Fruit Pectins Their Chemical Behavior and Jellying Properties (London: His Majesty's Stationery Office, Department of Scientific and Industrial Research Special Report 48, 1939), p. 23.



THE RELATIVE VISCOSITY AND CALCIUM PECTATE CONTENT
OF 0.2% APPLE AND GUAVA PECTIN SOLUTIONS

FIGURE 4

Pectins from the different varieties of apples and the guavas were all extracted following the described method. Chemical determinations were then made on the pectins thus obtained.

Table 8 indicates the results obtained for free acidity, total acidity, relative viscosity, calcium pectate content, saponification value and iodine reducing power determinations made on three samples of guava pectins and on Jonathan, Joan, Haralson, Hawkeye, Cortland and McIntosh apples. The results show close agreement between various extracts of the same fruit. Similar close agreement was obtained when gooseberry pectin or apple pectin determinations were made during preliminary work.

Calcium Pectate Determination

Solutions of approximately the same pectin content were prepared from each of the fruit pectins. Calcium pectate determinations were then made on each solution using the method described in the preceding experimental work on fruit extracts.

Relative Viscosity of Pectins

Relative viscosity measures using the Baker Ostwald viscosity pipette were made on each of the solutions used for the determination of calcium pectate.

The data given in Table 8 and graphed in Figure 4 indicate that there is a relationship between the calcium pectate, relative viscosity, and gelation properties of pectins from six varieties of apples and guava. The poorer gelation properties of guava pectin were indicated as it had a greater calcium pectate content in relation to its relative viscosity than did the apple pectins. Guava pectin solution of more than 0.280% calcium pectate content gave a relative viscosity of only 2.7 while apple extracts of 0.131 to 0.153 calcium pectate had a relative viscosity of 3.0 to 4.0. The McIntosh apple pectin solution, which had a relative viscosity value of 2.6 gave the highest calcium pectate content of the apples or that of 0.153. It will be recalled that the guava and McIntosh extracts were the ones which had the highest calcium pectate yields for corresponding relative viscosities and yet produced the weakest jellies.

It will be observed that the pectin solution made from different guava extracts of the same variety correlate rather

closely while there is a great variation among the different varieties of apples or between the apple and guava pectins.

TABLE 8
CHEMICAL PROPERTIES OF APPLE AND GUAVA PECTINS

No.	Fruit	0.2 Per Cent Solution		Free Acidity ^a	Total Acidity ^a	Iodine Reducing Power ^b	Saponification Value ^a
		Relative Viscosity	Calcium Pectate				
			per cent	gram	gram	per cent	gram
1	Guava	3.0	0.284	.83	18.2	15.4	8.2
2	Guava	2.7	0.296	.80	17.4	15.7	7.7
3	Guava	2.7	0.300	.90	17.2	16.1	8.2
	Apple						
4	Jonathan	3.4	0.146	.80	16.3	9.3	7.5
5	Cortland	3.5	0.136	.83	18.0	12.5	9.3
6	Hawkeye	4.0	0.136	.89	13.1	11.1	7.6
7	McIntosh	2.6	0.153	.85	15.4	12.0	7.2
8	Haralson	3.0	0.144	.92	18.6	11.7	8.5
9	Joan	2.5	0.104	.81	22.0	15.1	11.3

^aFree acidity, total acidity and saponification value expressed as grams of sodium hydroxide per 100 grams of pectin on the calcium pectate basis.

^bIodine reducing power expressed as percentage dextrose.

Free Acidity of Pectin Solutions

This determination, based on the well known fact that pectin is acidic in character was carried out by titrating a solution of pectin with 0.1N sodium hydroxide. The indicator was that suggested by Hinton¹ which changes at pH 7.5 which eliminates the possibility of a slight excess of alkali saponifying some of the ester groups of the pectin and thus giving high values.

It consists of the following mixture:

Bromo thymol blue	(0.4 per cent)	1 volume
Phenol red	(0.4 per cent)	3 volumes
Cresol red	(0.4 per cent)	1 volume
Distilled water		1 volume

The end point was taken when the red color persisted 30 seconds.

¹Op. cit., p. 27.

In Table 8 the free acidity of different pectin solutions are indicated with values ranging from 0.80-0.92 grams of sodium hydroxide per 100 grams of calcium pectate. There is no correlation between free acidity and the gelation properties of pectins.

Saponification Value of Pectins

Although the molecule of pectin is very complex, there is evidence that it contains free carboxyl groups and methoxy groups. The latter ones probably linked to the molecule as esters. Furthermore a number of carboxyl groups present in the molecule may have gone through neutralization by metallic bases to form in salts.

If such pectin solutions are carefully neutralized of free acidity it has been found that no hydrolysis of methoxy groups occurs. Saponification of the methoxy groups can then be carried out readily by alkali and the results obtained calculated as the saponification value of the pectin or an indirect determination of the approximate methoxyl content of the pectin.

Experimental details for the determination of the saponification values of pectins are those suggested by Hinton¹ and are essentially as follows:

A solution of pectin is carefully neutralized by the addition of decinormal sodium hydroxide using the special indicator already described in the determination of free acidity. The end point is taken when the red color persists one-half minute. Ten milliliters of half-normal sodium hydroxide are then added and the flask is stoppered and allowed to stand one-half hour. Excess of alkali is then titrated with decinormal hydrochloric acid. Blank determinations are made and the difference calculated as grams sodium hydroxide per 100 grams of pectin on the calcium pectate basis.

Saponification values obtained on the pectins studied are indicated in Table 8. No relationship could be established between the saponification value of the pectins and their gelation properties.

Total Acidity of Pectins

This value is a measure of the total acidity produced by all carboxyl groups in the pectin molecule whether they be free,

¹Ibid., p. 27.

esterified or neutralized. It is therefore independent of the partial neutralization or esterification of the different carboxyl groups.

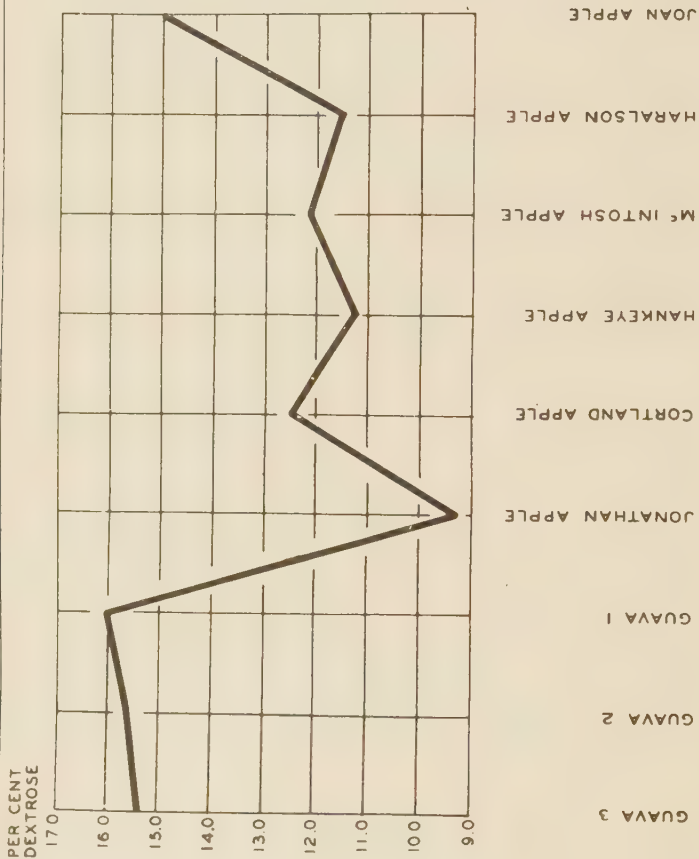
The determination is based on the fact that pectic acid is insoluble in acid solutions. If a neutral sodium pectate solution obtained by preliminary saponification of a pectin solution, followed by neutralization is treated with hydrochloric acid, the pectic acid is precipitated thus requiring a definite amount of hydrochloric acid. The pectic acid is then filtered, and the excess hydrochloric acid in that filtrate titrated with sodium hydroxide. Thus the precipitated pectic acid which is a measure of the total carboxyl groups can be expressed in terms of grams of sodium hydroxide per 100 grams of calcium pectate.

The experimental details of the method used for the determination of the total acidic groups of pectin, were those of Hinton¹ which are essentially as follows: To the neutralized solution remaining from the determination of the saponification value of pectins previously described is added 50 ml. of decinormal hydrochloric acid in order to precipitate the pectic acid. The flask is well shaken and placed in a boiling water bath for ten minutes in order to get the pectic acid in a more flocculent condition. The solution is cooled and made to volume, mixed well, and filtered. A large aliquot of the filtrate is then titrated with decinormal sodium hydroxide. A blank is treated in exactly the same way and the difference between the pectic acid determination and the blank calculated to the full volume and finally expressed in grams of sodium hydroxide per 100 grams of pectin on the calcium pectate basis. Data in Table 8 indicate variations in the total acidic groups of the different pectins. There is no relation between these values and the gelation properties of the extracts.

Iodine Reducing Power of Pectins

The pectin molecule as has been said is known to contain galacturonic acid groups linked together to form a suggested open chain with free aldehyde groups at the end. The reducing power for pectin is therefore a measure of the free aldehyde groups present, which in turn is inversely proportional to the length of

¹Ibid., p. 35.



THE IODINE REDUCING POWER OF APPLE AND GUAVA PECTINS
FIGURE 5

the chain. The important reactions from the analytical point of view and which serve for the calculation of the reducing power of pectins are: pectin reduces iodine and excess iodine is titrated with a thiosulphate solution. The experimental details for the determination of iodine reducing value of pectins as adapted from Hinton's method¹ is as follows:

To 50 ml. of a pectin solution in a 250 ml. flask are added 40 ml. of a 0.5 normal iodine solution followed by 5 ml. of a 0.4 normal sodium hydroxide. The flask is stoppered, allowed to stand for 15 minutes at room temperature, then acidified with 10 ml. dilute hydrochloric acid and the excess iodine titrated with 0.1 normal sodium thiosulphate.

A blank test is similarly carried out and the difference calculated as iodine reduced by the pectin solution. The iodine reducing power of the pectin is expressed as grams of dextrose that reduce the same amount of iodine as that reduced by one hundred grams of pectin on the calcium pectate basis.

The results obtained agree with those of other workers in that pectin units must be linked together as chains, leaving free aldehyde groups after condensation which have reducing properties.

Data in Table 8 graphed in Figure 5 indicate a marked difference in the iodine reducing power of the different pectins and a correlation between the iodine reducing power and gelation properties of apple and guava pectins.

Guava which produced the weakest jellies and those which had to be varied the most from Baker's suggested formula in order to obtain excellent products, had the highest iodine reducing power, while Jonathan apples, giving the best of all the jellies, had the lowest iodine reducing power.

All other apple pectins had decidedly lower iodine reducing values than guava pectin except Joan, whose extracts did produce weaker jellies on the whole in keeping with the higher iodine reducing value.

Although McIntosh jellies were the weakest as a whole, which as has been pointed out may have been due to lower final pectin concentrations, its pectin had iodine reducing value in the range of other apples.

In general it may be noticed that apples seem to have a

¹Ibid., p. 41.

lower iodine reducing power than guavas and that there is some correlation indicated between this property and the better gelation characteristics of apples as compared with guavas. These results agree with those of Hinton who found that the iodine reducing power of an orange pectin varied inversely with its gelation properties and that loss of jellying power caused an increase in iodine reducing power, suggesting cleavage of long chain molecules with a larger number of iodine reducing groups free.

In keeping with the relation which was found to exist between the iodine reducing power of a pectin and its gelation power only one other property studied pointed to the same conclusion, that molecular size of guava pectin was smaller than that of apple pectin. This is the relation of viscosity to pectin content expressed as calcium pectate; for example, the pectin of guava gave lower relative viscosities than apple pectins for approximately the same calcium pectate content, indicating that the weaker gelation properties of the guava pectin was due to smaller molecular size in the guava pectin as compared to that in apple pectin.

In view of the great variation obtained when a limited number of pectin preparations from guava and six varieties of apples were analyzed much more extensive work should be carried out in order to determine the relation of the chemical and physical properties of pectins and their gelation behavior.

SUMMARY

Considerable research has been undertaken in the past few years in order to determine the qualitative and quantitative relationship which exists among the three main constituents of gels; pectin, acid and sugar. The processes involved have been understood and formulas devised to assure excellent products of definite chemical composition usually based on a high final sugar concentration and purified or commercial pectins.

Prevailing conditions make it necessary, however, that experimental work be carried out to actually determine the adaptability of suggested formulas in the preparation of low sugar concentration products using natural fruit extracts and assuring besides a minimum sugar content, a maximum flavor and excellent texture.

The present research was undertaken with a threefold purpose: first to determine the quantitative relationship which exists among acid, pectin and sugar in the preparation of low sugar concentration products; second to determine if available formulae apply or can be made to apply in the preparation of low sugar concentration jellies from different fruits and different varieties of the same fruit; and finally to study the relation of several physical and chemical properties of the various fruit pectins to their gelation behavior.

Experimental Work with Synthetic Jellies

Synthetic jellies were prepared by using sucrose, 0.1 normal tartaric acid and citrus fruit pectin obtained from the California Fruit Grower's Association.

First a standard jelly was prepared which was considered excellent in that it held its angles when cut, was decidedly quivery and did not show syneresis or weeping.

Then the effect of varying the acid, sugar and pectin was observed by altering one of these factors gradually while maintaining the remaining two constant as in the standard. It was found that if any of the three factors are decreased from that proportion which results in an excellent jelly, the product obtained will be too weak or no jelly at all. Increased sugar or pectin made the jelly too tough, while increase in acid content caused little change within a rather wide limit, although finally resulting in syneresis.

Another set of experiments with the synthetic solutions was carried out to find whether or not the deficient products obtained in the previous set could be made excellent by compensation of one factor by another. This time the deficient factor was maintained constant and the others increased gradually.

When a jelly was slightly deficient in any one factor, increase of another factor compensated for the deficiency except in the case of a sugar deficient extract in which increase in pectin alone did not compensate for the deficiency.

In general all the experiments with synthetic jellies showed definitely that although with the quantities of two elements fixed there exists a limited range, that is a quantitative relationship of the remaining element among pectin, acid and sugar, which will produce a good jelly, no one definite proportion of

all three is required for gelation.

Experimental Work with Fruit Extracts

In order to determine if available formulae apply or can be made to apply in the preparation of low sugar concentration jellies of excellent quality from fruits, experimental work was carried on with guava and six varieties of apples (Joan, Jonathan, Haralson, Hawkeye, McIntosh and Cortland).

Extracts of varying relative viscosity were prepared from each of the fruits mentioned above, pH value adjusted within a range of 2.5 to 3.5 and 55 and 50 per cent sugar concentration gels prepared according to formulas. Some were prepared following Baker viscosity formula basing the sugar holding capacity of extracts on the relative viscosity the formula being

$$\log \text{ of viscosity} = ax + b$$

$$\text{when } a = .675$$

$$b = .236$$

and x is the amount of sugar to be added per part of extract.

Others were prepared by using two adaptations of the formula as follows: Instead of adding the calculated amount of sugar to be added per part of extract, as indicated by the formula, only 87.5 per cent or 75 per cent of the calculated added sugar was used but the mixture boiled down to the same final sugar concentration of 55 per cent or 50 per cent. These two variations offered a greater concentration of extract in the final product.

Pectin determinations in terms of calcium pectate were made in all extracts, using the combination alcohol and calcium pectate method.

Finished products were subjectively compared by use of a score card. The gels were likewise tested objectively by means of a jelly strength tester designed by the Delaware Agricultural Experiment Station which measures the strength of gels as centimeters of water pressure required to break the surface.

The results obtained support several previous contentions in relation to the quantitative and qualitative relationship among pectin acid and sugar. Among these are the following.

1. Excellent products are obtained from a most varied combination of pectin acid, and sugar.

2. In a slightly deficient extract compensation of the deficient factor may be obtained by addition of an excess of a second factor.
3. Relative viscosity is a measure of the strength of a pectin solution thus resulting from a combination of the quality and quantity of pectin in an extract.
4. The greater the hydrogen ion concentration of an extract the greater the sugar holding capacity.

However, results obtained indicated that although there is a limiting value of pH for a particular extract, under a definite set of conditions, there is a most varied range of pH for gelation of different fruits or even different extracts of the same fruit. That is to say that there is evidently no optimum pH value for gelation but a most varied range of acidity depending on the sugar concentration, fruit being used, and other factors.

Results indicate a definite wide variation in the gelation properties of guava and apple extract. Pectin in guava is much weaker, of poorer quality and apparently of lower molecular weight than that from apples. This is indicated by the fact that a smaller amount of apple pectin gave the same relative viscosity as that obtained with a guava extract of a high content of pectin. At all times the strength of guava gels was much less than that of gels prepared from apple extracts of corresponding relative viscosity. This supports the previous contention that guava pectin is weaker and of poorer gelation properties.

Due to this difference, excellent products could be prepared from guavas by using Baker's formula. Only when the variation of 75 per cent of the calculated sugar per part of extract was used could excellent products be obtained.

Not only is there a great variation between the gelation properties of guava and apple pectins but likewise a great variation among the different varieties of the same fruit as indicated by the results on the six varieties of apples.

Extracts from different apples having identical relative viscosity had different calcium pectate content.

Joan extracts for example appear to contain weaker pectins than other apples both by the criterion of calcium pectate content as related to relative viscosity of the extract and by the theory that its higher iodine value indicates lower molecular weight. This was not true of McIntosh extracts although the jellies from

the latter were even weaker than those from Joan. The weak McIntosh jellies would seem to be explained by a lower final concentration of pectin rather than by a weak pectin. This indicates that all varieties of apples do not have the same quality of pectin.

Wide variation was obtained in the jelly strength of the products prepared. The McIntosh apples gave the weakest products while those from other apples, especially Haralson, were much stronger. Jelly strength measurements obtained varied with the fruit or variety of fruit, with the pH and the relative viscosity of the extract.

Baker's formula gave 55 per cent sugar concentration products considered excellent and selected as first choice only for the Haralson extracts. Best results for the other varieties of apples we obtained when the variation of 87.5 per cent of calculated amount of sugar per part of extract was used. Products considered second choice for Jonathan, Cortland and Joan apples were prepared by following Baker's formula, while the same proportion resulted in too weak or soft products when applied to McIntosh and Hawkeye extracts. Second choice for these two apples were those products prepared by the 75 per cent sugar variation. All Haralson products of 55 per cent sugar concentration prepared from any formula or variation not Baker's produced gels too firm or tough.

In general Jonathan apple pectin was considered to be the most satisfactory and have the best gelation properties of all fruits tested, for the preparation of low sugar concentration gels. Excellent 55 per cent sugar concentration products were obtained with either the 87.5 per cent, 75 per cent variation, or the Baker's formula. With all other varieties of apples and guava, such a wide variation in proportions resulted in poor gels.

Some excellent 50 per cent sugar concentration gels were prepared from all varieties of apples using 87.5 per cent variation. However, 50 per cent sugar concentration gels could only be prepared from guavas if low viscosity extracts were used and the 75 per cent sugar variation.

Structure of Pectin Gels

Attempts to correlate the gelation properties of fruit extracts to their suggested structural network formation were un-

successful. No pectin structure could be observed through the use of a slit-untramicroscope. This does not imply that no such structure exists but more likely that the structure is not visible through the available apparatus.

Chemical Properties of Pectins

Experiments were then undertaken to find any possible correlation among the chemical and gelation properties of fruit pectins. Pectins were extracted from the six varieties of apples and from guava. They were purified by resolution and reprecipitation with acetone and observations made on their chemical properties and variations.

Free acidity, total acidity, saponification value, relative viscosity and iodine reducing power of pectins were determined.

No correlation was obtained between the gelation behavior and the following chemical properties: free acidity, total acidity, or saponification number. It is only when we come to the figures for relative viscosity and iodine reducing power of the pectins that there is evidence of a correspondence with gelation properties.

High pectin content of guava solution gave a correspondingly low viscosity, while a low pectin content of apple solution gave a high relative viscosity measurement. This observation correlates with the weak quality of the pectin from guava as compared with the apple extracts.

Iodine reducing power was approximately in the inverse order of gelation properties. Guava pectin having poor gelation characteristics had high iodine reducing power while Jonathan apples which produced the best low sugar concentration gels had the lowest iodine value. Both iodine reducing power and relative viscosity values indicate a possibly lower molecular weight pectin for guava as compared with apple.

Due therefore to the wide difference in gelation properties exhibited by the guava and apple pectins and even by six different varieties of apples, formulas at present available must be adapted before they are satisfactorily used for the preparation of low sugar concentration products. In view of the experimental results, 55 per cent sugar concentration gels of excellent quality and flavor, can be prepared from both guava and apples if formula

are adapted. Acid either in the form of tartaric acid or lemon juice must be added, and formula varied so that only 87.5 per cent of calculated sugar per part of extract is used for apples and 75 per cent calculated sugar per part of extract is used for guava. Both the change in proportions and the increase in acid will alter the pectin acid and sugar relation in the final product and result in excellent gels.

It is unquestionably not enough to select a fruit merely for its pectin content as in the case of guavas if low sugar concentration products are to be prepared. Both quality and quantity of pectin must be considered, and formulas adopted to the particular fruit and even to the particular variety of fruit to be used. These were clearly indicated by the great variation in gelation behavior of guava and apple pectins and among six varieties of apples.

